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(54) POSITIVE ELECTRODE ACTIVE MATERIAL FOR LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive electrode active material for lithium secondary battery and a method to manufacture the active material, assuring a high battery capacity, mean discharge voltage, charge-discharge cyclic durability, and the safety.

SOLUTION: A positive electrode active material for a lithium secondary battery is formed from a lithium-containing compound oxide expressed by LiNixCoyMzO_2 , where M is either of Al, Mn, Ti, Mg, Cr, and the conditions should be met that $0.95 \leq x+y+z \leq 1.05$, $0.5 \leq x \leq 0.9$, $0.05 \leq y \leq 0.3$, and $0 \leq z \leq 0.2$, wherein the half-value width of the diffraction peak at $2\theta = 65 \pm 1^\circ$ in X-ray diffraction should range between 0.13° and 0.20° .

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CLAIMS

[Claim(s)]

[Claim 1] A general formula, $\text{LiNi}_x\text{Co}_y\text{M}_z\text{O}_2$ (however, M) At least one sort of elements chosen from aluminum, Mn, Ti, Mg, and Cr, It is expressed with $0.95 \leq x+y+z \leq 1.05$, $0.5 \leq x \leq 0.9$, $0.05 \leq y \leq 0.3$, and $0 \leq z \leq 0.2$. And positive active material for lithium secondary batteries characterized by the diffraction full width at half maximum based on the field in $2\theta = 65^\circ$ (110) of the powder X diffraction which used CuK alpha rays consisting of a lithium content multiple oxide which is 0.13-0.20 degrees.

[Claim 2] A general formula, $\text{LiNi}_x\text{Co}_y\text{M}_z\text{O}_2$ (however, M) At least one sort of elements chosen from aluminum, Mn, Ti, Mg, and Cr, It is expressed with $0.95 \leq x+y+z \leq 1.05$, $0.5 \leq x \leq 0.9$, $0.05 \leq y \leq 0.3$, and $0 \leq z \leq 0.2$. And the diffraction full width at half maximum based on the field in $2\theta = 65^\circ$ (110) of the powder X diffraction which used CuK alpha rays The salt or coprecipitate containing the salt which is the manufacture approach of the positive active material for lithium secondary batteries which consists of a lithium content multiple oxide which is 0.13-0.20 degrees, and contains nickel and cobalt, a coprecipitate or nickel, cobalt, and Element M, The manufacture approach of the positive active material for lithium secondary batteries which carries out preceding paragraph baking of mixture with a lithium compound, or the mixture of a lithium compound and the compound containing Element M at 430-530 degrees C, and is subsequently characterized by carrying out latter-part baking at 700-850 degrees C.

[Claim 3] The manufacture approach of the positive active material for lithium secondary batteries according to claim 2 that the temperature fall rate of preceding paragraph baking is 200-600 degrees C/o'clock.

[Claim 4] The manufacture approach of the positive active material for lithium secondary batteries according to claim 2 or 3 that the temperature fall rate of latter-part baking is 100-500 degrees C/o'clock.

[Claim 5] The manufacture approach of the positive active material for lithium secondary batteries according to claim 2, 3, or 4 that latter-part baking is performed by roller HASU kiln at least.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the new positive active material for lithium secondary batteries which consists of a lithium content multiple oxide, and its manufacture approach.

[0002]

[Description of the Prior Art] The expectation for small, the nonaqueous electrolyte rechargeable battery which is lightweight and has a high energy consistency, especially a lithium secondary battery is growing as portable-izing of a device and cordless-ization progress in recent years. The multiple oxide of lithiums, such as LiCoO_2 , LiNiO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, LiMn_2O_4 , and LiMnO_2 , and transition metals is known by the positive active material for lithium secondary batteries. The lithium secondary battery which used for positive active material the rock salt stratified multiple oxide which made cobalt and nickel dissolve like $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ shows good reversibility in high electrical-potential-difference regions, such as 2.7-4.3V, while being able to attain 180 - 190 mAh/g and a comparatively high capacity consistency.

[0003] Adoption of the lithium-nickel-cobalt multiple oxide represented by $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ has started as an ingredient which can especially discover high capacity recently. These are used for positive active material and commercialization of the lithium secondary battery of the high voltage by using occlusion, the carbon material which can be emitted as a negative-electrode active material, and a high energy consistency is advanced in the lithium.

[0004] Conventionally as the manufacture approach of a rock salt stratified multiple oxide of having made cobalt and nickel dissolving like $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ A nickel-cobalt coprecipitate is mixed with a lithium compound. At a standing furnace The inside of air, How to heat at 920 degrees C for 3 hours (JP,1-129364,A), Mix a nickel-cobalt coprecipitate with a lithium compound and a temperature up is carried out the rate for 330-degree-C/using rotary kiln. The approach lower the temperature and a standing furnace performs this baking at 750 degrees C under an oxygen ambient atmosphere further for 4 to 20 hours after performing preliminary baking (JP,11-111290,A), After it mixes a nickel-cobalt coprecipitate with a lithium compound and a standing furnace performs preliminary baking at 500 degrees C for 5 hours, the temperature is lowered and the approach (JP,10-214624,A) a standing furnace performs this baking at 720 degrees C under an oxygen ambient atmosphere further for 10 hours etc. is proposed.

[0005] However, by the approach of perform preliminary baking or this baking using rotary kiln, since mixing of impurities, such as an alumina which be a wall ingredient by wear of rotary kiln in order to make solid-state powder flow within rotary kiln, be avoid, there be problems, such as elevated temperature degradation of wall ingredients, such as a problem that the charge and discharge cycle endurance of the lithium secondary battery which used the baking object for the

active material be scarce, and an alumina of rotary kiln.

[0006] Moreover, by the industrial scale production which requires calcinating so much at once for a productivity drive, when a standing furnace performs preliminary baking or this baking, in order to lessen the problem which a lithium content multiple oxide with a sufficient property cannot manufacture easily since the temperature variation in the temperature up of solid-state powder and the lot at the time of a temperature fall is not avoided, and temperature variation, it is necessary to make small a temperature up or a temperature fall rate. Consequently, a temperature up and temperature fall time amount become long, and there is a problem to which productivity falls remarkably.

[0007] Moreover, a proposal that it excels in high capacity and thermal stability also has the lithium content multiple oxide whose diffraction full width at half maximum based on the field in the X diffraction (003) which mixes the alkali coprecipitation hydroxide and lithium hydroxide of nickel salt and cobalt salt, heat-treats, and is acquired is 0.01-0.1 degrees (JP,9-129231,A). However, even if it was the lithium content multiple oxide with which it is obtained by the manufacture approach given [this] in an official report, and (003) the diffraction full width at half maximum based on a field has the above-mentioned range, capacity, a discharge average electrical potential difference, charge-and-discharge cycle endurance, and safety were still dissatisfied.

[0008]

[Problem(s) to be Solved by the Invention] As mentioned above, the lithium content multiple oxide manufactured by the conventional approach needed the further amelioration as positive active material for lithium secondary batteries in the initial capacity, the initial discharge average electrical potential difference, the charge-and-discharge cycle endurance, the safety, and productivity of a cell.

[0009] This invention has a big cell capacity, its discharge average electrical potential difference is high, is excellent in charge-and-discharge cycle endurance, and aims at offering the new positive active material for lithium secondary batteries which consists of a high lithium content multiple oxide and its manufacture approach of safety.

[0010]

[Means for Solving the Problem] this invention person found out that the lithium content multiple oxide with which the diffraction full width at half maximum based on a field (110) in $2\theta = 65^\circ$ of the powder X diffraction which was expressed with the specific general formula and used CuK alpha rays has a specific value satisfied both a high initial cell capacity a high discharge average electrical potential difference the outstanding charge-and-discharge cycle endurance and high safety as positive active material of a lithium secondary battery.

[0011] In this way, this invention is a general formula and LiNixCoyMzO_2 (however, M). At least one sort of elements chosen from aluminum, Mn, Ti, Mg, and Cr, It is expressed with $0.95 \leq x+y+z \leq 1.05$, $0.5 \leq x \leq 0.9$, $0.05 \leq y \leq 0.3$, and $0 \leq z \leq 0.2$. And the diffraction full width at half maximum based on the field in $2\theta = 65^\circ$ (110) of the powder X diffraction which used CuK alpha rays is in the positive active material for lithium secondary batteries characterized by consisting of a lithium content multiple oxide which is 0.13-0.20 degrees.

[0012] Below, this invention is explained further at a detail.

[0013]

[Embodiment of the Invention] In this invention, the lithium content multiple oxide which constitutes the positive active material of a lithium secondary battery is expressed with a general formula and LiNixCoyMzO_2 . In here, M is a kind of element chosen from aluminum, Mn, Ti, Cr, and Mg at least. x, and y and z are chosen, respectively so that $0.95 \leq x+y+z \leq 1.05$, $0.5 \leq x \leq 0.9$, $0.05 \leq y \leq 0.3$, and $0 \leq z \leq 0.2$ may be satisfied.

[0014] In the above, even when M is not contained by $z = 0$, the initial capacity of a cell is high

and its charge-and-discharge cycle stability is high. z is not 0, when M is aluminum, compared with additive-free [of M] ($z=0$), the charge-and-discharge cycle stability of a cell is still higher, there are few capacity falls in rapid charge and discharge, exoergic temperature is high, and safety is still higher. z is not 0, when M is Mn, compared with additive-free [of M], the exoergic temperature of a cell is high and safety is still higher. Furthermore, z is not 0, when M is Ti, Cr, or Mg, compared with additive-free [those], the charge-and-discharge cycle stability of a cell is high, and discharge voltage is also high. Especially, in this invention, a kind of element of aluminum and Mn of M is desirable at least.

[0015] In the above, the initial capacity of a cell falls that x is less than 0.5 about x , and y and z . If 0.9 is exceeded, the thermal stability of a cell will fall or charge-and-discharge cycle endurance will fall. Preferably, it is $0.60 \leq x \leq 0.85$. Since the thermal stability of a cell falls that y is less than 0.05 or charge-and-discharge cycle endurance falls, it is not desirable. If 0.3 is exceeded, the initial capacity of a cell will fall. Preferably, it is $0.10 \leq y \leq 0.20$. Moreover, although z is based also on an alloying element, it is $0.005 \leq z \leq 0.10$ preferably.

[0016] Moreover, in the powder X diffraction for which the lithium content multiple oxide which is the positive active material of this invention used CuK alpha rays, the diffraction full width at half maximum based on a field (110) in $2\theta = 65^\circ \pm 1$ degree has 0.13-0.20 degrees. (110) It is thought that the diameter of microcrystal has the relation it is small unrelated, so that the diffraction full width at half maximum based on a field has large half-value width reflecting the diameter of microcrystal of a lithium content multiple oxide. (110) The charge-and-discharge cycle endurance of the cell used as positive active material as the diffraction full width at half maximum based on a field is less than 0.13 degrees, initial capacity, average discharge voltage, or safety falls. Moreover, if the diffraction full width at half maximum based on a field (110) exceeds 0.20 degrees, the initial capacity of a cell and safety will fall. Desirable half-value width is 0.14-0.17 degrees.

[0017] The lithium content multiple oxide which has the general formula and the specific X diffraction full width at half maximum of the above-mentioned specification in this invention is the following, and making and manufacturing is desirable. That is, preceding paragraph baking of the mixture of the salt or coprecipitate containing the salt containing nickel and cobalt, a coprecipitate or nickel, cobalt, and Element M , and a mixture with a lithium compound or a lithium compound and the compound containing Element M is carried out at 430-530 degrees C, and, subsequently latter-part baking is carried out at 700-850 degrees C. In the above, when Element M is not contained in a lithium multiple oxide, the mixture of the salt or coprecipitate containing nickel and cobalt, and a lithium compound is calcinated (when it is $z=0$).

[0018] When nickel, cobalt, and Element M are contained in the salt or coprecipitate containing the salt containing the above-mentioned nickel and cobalt, a coprecipitate or nickel, cobalt, and Element M , it is desirable that nickel, cobalt, and Element M are distributed over homogeneity. Moreover, with the salt containing the salt and nickel containing nickel and cobalt, cobalt, and Element M , a carbonate, a sulfate, a nitrate, complex salt, etc. are used preferably.

[0019] The salt or coprecipitate containing the salt containing these nickel and cobalt, a coprecipitate or nickel, cobalt, and Element M is preferably manufactured by the following approaches. for example, when a nickel chloride, a cobalt chloride, and Element M are included Each chloride of Element M is made to dissolve in the water solution which saturated carbon dioxide gas. When the approach of adding and carrying out coprecipitation of the sodium-hydrogencarbonate solution, and drying it, the same nickel as the above, cobalt, and Element M are included 100-150 degrees C is made to heat the ammine complex mixed water solution containing Element M by the pressure of one to 5 atmospheric pressure the approach and nickel which are made to add and carry out coprecipitation of the alkali to the water solution containing each chloride of Element M , and are dried, cobalt, and if needed, and the approach of drying is

adopted.

[0020] The approach of mixing the water solution which contains the salt or coprecipitate containing nickel and cobalt, and the compound of Element M when not using the salt or coprecipitate containing nickel, cobalt, and Element M, mixing a lithium compound further, and above, drying by the case where Element M is contained in a lithium content multiple oxide, is adopted preferably. Moreover, even when using the salt or coprecipitate containing nickel, cobalt, and Element M, it may mix with the water solution which contains the compound of Element M further, and Element M may be filled up. As a lithium compound mixed to the salt or coprecipitate containing the element M contained nickel, cobalt, and if needed, a lithium hydroxide, a lithium carbonate, lithium oxide, etc. are used preferably.

[0021] Subsequently the mixture of the salt or coprecipitate which contains Element M by this invention nickel, cobalt, and if needed, and a lithium compound is calcinated. It is required to perform baking by preceding paragraph baking in a specific temperature requirement and latter-part baking of each above. Baking of the preceding paragraph and the latter part may be plural [two or more steps of], respectively. If one of one-step baking is performed instead of two-step baking with the above-mentioned preceding paragraph and the latter part, the property used as the positive active material of the obtained lithium content multiple oxide, the initial capacity which is specifically a cell, charge-and-discharge cycle endurance, safety, average discharge voltage, etc. will fall. Even if it is in two-step baking, when the temperature of preceding paragraph baking exceeds less than 430 degrees C or 530 degrees C or the temperature of latter-part baking exceeds less than 700 degrees C or 850 degrees C, the property as positive active material of the lithium content multiple oxide obtained like the above, i.e., initial capacity, charge-and-discharge cycle endurance, safety, average discharge voltage, a rapid charge-and-discharge property, etc. fall.

[0022] Moreover, it is desirable that the holding time [in / in preceding paragraph baking / the above-mentioned burning temperature] is 0.3 - 3 hours in this invention, and 0.5 - 2 hours is especially suitable. Moreover, the temperature fall rate (rate at which the temperature of a furnace descends from burning temperature to 200 degrees C) in preceding paragraph baking has desirable o'clock in 200-600 degrees C /, and o'clock is suitable for it in 300-500 degrees C /especially. The reaction of the powder and lithium compound which make nickel and cobalt a subject to preceding paragraph firing time being less than 0.3 hours is inadequate, and since the initial capacity of the lithium secondary battery using the obtained lithium content multiple oxide as positive active material falls, it is not desirable. On the other hand, if firing time exceeds 3 hours, since the productivity of a cell will fall, it is not desirable. It becomes [the diameter of a crystal of a lithium content multiple oxide] large that this temperature fall rate is less than 200 degrees C/o'clock to that programming rate hardly doing effect in preceding paragraph baking and is not desirable. Since a quick cooling facility is needed in large scale production when a temperature fall rate exceeds o'clock in 600 degrees C /and an installation cost and a running cost become high on the other hand, it is not desirable. Furthermore, as for latter-part baking, it is desirable that the holding time in the above-mentioned burning temperature is 1 - 4 hours in this invention, and 1 - 2.5 hours is suitable for it especially. Moreover, the temperature fall rate (rate at which the temperature of a furnace descends from burning temperature to 200 degrees C) in latter-part baking has desirable o'clock in 100-500 degrees C /, and o'clock is suitable for it in 200-400 degrees C /especially. Since the shift reaction to the layer structure containing the lithium of the powder and lithium compound which make nickel and cobalt a subject to the above-mentioned firing time being less than 1 hour is inadequate, it is not desirable. When the above-mentioned firing time exceeds 4 hours, as a result of a crystal's growing on the other hand, since the engine performance as positive active material of the obtained lithium content multiple oxide falls and the productivity of a lithium content multiple oxide falls, it is not desirable. To

that programming rate hardly doing effect, the diameter of a crystal of a lithium content multiple oxide size-comes that this temperature fall rate is less than 100 degrees C/o'clock, and latter-part baking also comes. Since a quick cooling facility is needed in large scale production when a temperature fall rate exceeds o'clock in 300 degrees C /or more and an installation cost and a running cost become high on the other hand, it is not desirable.

[0023] It is desirable to perform above-mentioned preceding paragraph baking and above-mentioned latter-part baking in oxygen content gas, and although especially the oxygen density in preceding paragraph baking is not made an issue of, it is appropriate for it to carry out in atmospheric air. On the other hand, as for latter-part baking, it is desirable to carry out in the high oxygen content gas of an oxygen density. The oxygen density of latter-part baking has desirable 19 - 100 volume %, and 25 - 50 volume % is especially suitable for it. Since the engine performance as positive active material of the lithium content multiple oxide obtained when the oxygen density in this latter-part baking was low falls, it is not desirable.

[0024] As a means to carry out the above-mentioned preceding paragraph baking and latter-part baking of this invention on a scale of industry, although rotary kiln, a continuous furnace, a roller hearth kiln, etc. are mentioned, rotary kiln is deficient in the endurance of the mixing problem to the product of the component, or a kiln wall by wear of a kiln wall, and since there is a dust processing problem in an outlet in being rapid baking, it is not desirable. In processing a lot of fine particles on a scale of industry, as a result of being hard to make temperature distribution into homogeneity, since the engine performance as positive active material of the obtained lithium content multiple oxide is inferior, a continuous furnace is not desirable.

[0025] On the other hand, a roller hearth kiln is equipment which is filled up with the powder which should be calcinated to the sheath which consists of refractories, throws a sheath into a tunnel-like furnace continuously, and carries out continuation baking of the rotation roller top when a sheath moves. Also in a rapid temperature up or a rapid temperature fall, a roller hearth kiln is excellent in especially the property as positive active material of the lithium content compound oxidation acquired since the temperature distribution in a sheath were made to homogeneity, and since productivity is high, it is desirable. Since this has uniform temperature distribution, it is because the diameter of average microcrystal is controllable. Although it is suitable for each of preceding paragraph baking and latter-part baking to carry out by the roller hearth kiln, it is appropriate preferably the either and to carry out latter-part baking by the roller hearth kiln.

[0026] In this invention, the positive electrode used as the positive active material of the above-mentioned lithium content multiple oxide is manufactured as follows preferably. namely, the thing for which carbon system electric conduction material and binding material, such as acetylene black, a graphite, and KETCHIEN black, are mixed to the powder of the above-mentioned lithium content multiple oxide -- a positive electrode -- a mixture is formed.

[0027] the above-mentioned positive electrode -- a mixture and this positive electrode -- a mixture -- the slurry or kneading object which consists of the inner solvent or inner dispersion medium of binding material -- positive-electrode charge collectors, such as aluminium foil and a stainless steel foil, -- spreading -- and/or, you make it support and it considers as a positive-electrode plate. Polyvinylidene fluoride, polytetrafluoroethylene, a polyamide, a carboxymethyl cellulose, acrylic resin, etc. are used for binding material. Porosity polyethylene, a porosity polypropylene film, etc. are used for a separator.

[0028] As a solvent of the electrolytic solution used for the lithium secondary battery which uses the lithium content multiple oxide of this invention as positive active material, a carbonate is desirable. a carbonate -- the shape of annular and a chain -- all can be used. As an annular carbonate, propylene carbonate, ethylene carbonate (henceforth EC), etc. are illustrated. As a chain-like carbonate, dimethyl carbonate, diethyl carbonate (henceforth DEC), ethyl methyl

carbonate, methylpropyl carbonate, methyl isopropyl carbonate, etc. are illustrated.

[0029] In this invention, it is independent about the above-mentioned carbonate, or two or more sorts can be mixed and used. Moreover, you may use it, mixing with other solvents. Moreover, if a chain-like carbonate and an annular carbonate are used together depending on the ingredient of a negative-electrode active material, a discharge property, cycle endurance, and charge-and-discharge effectiveness may be improvable. Moreover, it is good also as a gel polymer electrolyte by adding the solute which adds a vinylidene fluoride-hexafluoropropylene copolymer (for example, "KAINA" Atochem trade name) and the vinylidene fluoride-perfluoro (propyl vinyl ether) copolymer indicated by JP,10-294131,A, and carries out a postscript to these organic solvents.

[0030] It is desirable to use any one or more sorts of the lithium salt which makes an anion ClO_4^- , CF_3SO_3^- , BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , CF_3CO_2^- , $2(\text{CF}_3\text{SO}_2)\text{N}^-$, etc. as a solute which constitutes the electrolytic solution used for this invention. As for an above-mentioned electrolytic solution or an above-mentioned polymer electrolyte, it is desirable to add the electrolyte which consists of lithium salt by the concentration of 0.2-2.0 mols/l. to said solvent or a solvent content polymer. If it deviates from this range, ionic conductivity will fall and the electrical conductivity of an electrolytic solution will fall. L. is especially selected in 0.5-1.5 mols /preferably.

[0031] The negative-electrode active material in the lithium secondary battery of this invention is the ingredient which emits [occlusion and] a lithium ion. Although especially the ingredient that forms these negative-electrode active materials is not limited, carbon compounds, such as an oxide which made the subject the metal of 14 or 15 groups of a lithium metal, a lithium alloy, a carbon material, and the periodic table, for example, a silicon carbide compound, and a boron carbide compound, a silicon oxide compound, a titanium sulfide, etc. are mentioned. As a carbon material, the pyrolysis object of the organic substance, an artificial graphite, a natural graphite, an earthy graphite, expanded graphite, a scale-like graphite, etc. can be used. Moreover, the compound which makes the tin oxide a subject can be used as an oxide. Copper foil, a nickel foil, etc. are used as a negative-electrode charge collector.

[0032] When an active material is a carbon material etc., as for the negative electrode used by this invention, it is desirable to knead with an organic solvent, to consider as a slurry, to apply, dry or press and to manufacture this slurry to a metallic foil charge collector. There is especially no constraint in the configuration of a lithium cell. The shape of a sheet (the shape of so-called film), the letter of folding, a winding mold closed-end cylindrical shape, a carbon button form, etc. are chosen according to an application.

[0033]

[Example] Although an example explains this invention concretely below, this invention is not limited to these examples. In addition, Example 6 - Example 8 are examples of a comparison of this invention.

[Example 1] Each ammine complex of cobalt was mixed with nickel, the nickel which heated this at 100-150 degrees C under the pressure of one to 5 atmospheric pressure, and was obtained, the salt (atomic ratio 0.8:0.2 of nickel:Co) containing cobalt, and lithium-hydroxide 1 hydrate powder were mixed, and the sheath (at outside **, it is die-length [of 300mm] x width-of-face [of 300mm] x height of 80mm) which consists of mullite-cordierite system refractories was filled up. The above-mentioned sheath with which it filled up with raw material powder was continuously supplied to the roller hearth kiln (the overall length of 15m, height of 1.8m, width of face of 1.8m), was held at 515 degrees C for 30 minutes, and preceding paragraph baking was performed. The temperature fall time amount from 100 degrees C /and 515 degrees C to 200 degrees C of the programming rate from a room temperature to 515 degrees C was 40 minutes (470 degrees C/o'clock in temperature fall rate) o'clock.

[0034] After preceding paragraph baking, fine particles were taken out from the sheath and the sheath was again filled up with the fine particles after preceding paragraph baking after re-mixing. Using the same roller hearth kiln as the above, a temperature-distribution setup from an inlet port to an outlet and the speed of supply of a sheath were changed, the sheath was supplied continuously, under the oxygen-nitrogen air current containing oxygen 40 volume %, it held at 770 degrees C for 1.5 hours, and latter-part baking was performed. The temperature fall rate from 400 degrees C and 770 degrees C to 200 degrees C of the programming rate from a room temperature to 770 degrees C was 350 degrees C/o'clock o'clock.

[0035] Thus, about 0.20OLiNi0.80Co2 obtained powder, the X diffraction was measured by CuKalpha using Rigaku RINT2100 mold X-ray diffractometer. The diffraction full width at half maximum based on a field (110) in $2\theta=65^{\circ}$ of this X diffraction was 0.148 degrees.

[0036] The 0.20OLiNi0.80Co2 above-mentioned powder, acetylene black, and polytetrafluoroethylene powder were mixed by the weight ratio of 80/16/4, and it kneaded, fabricated and dried, adding toluene, and the positive-electrode plate with a thickness of 150 micrometers was manufactured. Aluminium foil with a thickness of 20 micrometers is used as a positive-electrode charge collector, a metal lithium foil with a thickness of 500 micrometers is used for a separator at a negative electrode using porosity polypropylene with a thickness of 25 micrometers, a nickel foil with a thickness of 20 micrometers is used for a negative-electrode charge collector, the solution which contains LiPF6 in the mixed solvent of EC and DEC1:1 by the concentration of one mol is used for the electrolytic solution, and it is ***** in an argon glove compartment about the simple sealing cel (cell) made from stainless steel.

[0037] The above-mentioned cel was charged to 4.3V by the positive-electrode area per two and 0.2mA of constant current of 1cm, and while discharging to 2.5V in 0.2mA of constant current and calculating initial discharge capacity subsequently, the charge-and-discharge cycle trial was performed 20 times. The initial discharge capacity in 2.5-4.3V was 198 mAh/g, the initial discharge average electrical potential difference was 3.777V, and the capacity after a 20 times charge-and-discharge cycle was 198 mAh/g. Moreover, similarly, it charged to 4.3V by the positive-electrode area per two and 0.2mA of constant current of 1cm, the simple sealing cel made from stainless steel was disassembled in the argon glove compartment, the positive-electrode object sheet after charge was taken out, and it pierced in 3mm of diameters after washing the positive-electrode plate, and sealed to the aluminum capsule with EC, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 186 degrees C.

[Example 2] It dried, after mixing each ammine complex of cobalt with nickel and mixing the nickel obtained by making 100-150 degrees C heat this under the pressure of one to 5 atmospheric pressure, the salt containing cobalt, and an aluminium nitrate water solution, and fine particles were obtained by calcinating at 300 degrees C for 5 hours. Lithium-hydroxide 1 hydrate powder was mixed with these fine particles, the sheath with which the same roller hearth kiln as Example 1 was filled up with raw material powder was supplied continuously, and preceding paragraph baking and latter-part baking were performed on the same conditions as Example 1.

[0038] The X diffraction chart was measured about 0.03OLiNi0.8Co0.17aluminum2 obtained powder like Example 1. In this X diffraction, the diffraction full width at half maximum based on the field (110) near $2\theta=65^{\circ}$ was 0.168 degrees.

[0039] The cell engine performance was evaluated like Example 1 using the 0.03OLiNi0.8Co0.17aluminum2 above-mentioned powder. Consequently, the initial discharge capacity in 2.5-4.3V was 188 mAh/g, the initial discharge average electrical potential difference

was 3.770V, and the capacity after a 20 times charge-and-discharge cycle was 185 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured.

Consequently, exoergic initiation temperature was 192 degrees C.

[Example 3] It dried, after mixing the nickel-cobalt coprecipitation hydroxide and manganese nitrate water solution which heated and obtained the coprecipitate to which coprecipitation of the water solution containing each chloride of nickel and cobalt was carried out with alkali, and fine particles were obtained by calcinating at 300 degrees C for 5 hours.

[0040] Lithium-hydroxide 1 hydrate powder was mixed with these fine particles, the sheath with which the same roller hearth kiln as Example 1 was filled up with raw material powder was supplied continuously, and preceding paragraph baking and latter-part baking were performed on the same conditions as Example 1. About 0.06OLiNi_{0.76}Co_{0.18}Mn₂ obtained powder, like Example 1, CuK alpha rays were used and the X diffraction was measured. The diffraction full width at half maximum based on a field (110) in 2theta=65**1 degree of this X diffraction was 0.161 degrees.

[0041] The cell engine performance was evaluated like Example 1 using the 0.06OLiNi_{0.76}Co_{0.18}Mn₂ above-mentioned powder. Consequently, the initial discharge capacity in 2.5-4.3V was 183 mAh/g, the initial discharge average electrical potential difference was 3.767V, and the capacity after a 20 times charge-and-discharge cycle was 183 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured.

Consequently, exoergic initiation temperature was 188 degrees C.

[Example 4] It dried, after mixing the nickel-cobalt coprecipitation hydroxide and nitric-acid titanium water solution which heated and obtained the coprecipitate to which coprecipitation of the water solution containing each chloride of nickel and cobalt was carried out with alkali, and fine particles were obtained by calcinating at 300 degrees C for 5 hours.

[0042] Lithium-hydroxide 1 hydrate powder was mixed with these fine particles, the sheath with which the same roller hearth kiln as Example 1 was filled up with raw material powder was supplied continuously, and preceding paragraph baking and latter-part baking were performed on the same conditions as Example 1. Make it be the same as that of Example 1 about 0.03OLiNi_{0.75}Co_{0.22}Ti₂ obtained powder. CuK alpha rays were used and the X diffraction was measured. The diffraction full width at half maximum based on a field (110) in 2theta=65**1 degree of this X diffraction was 0.162 degrees.

[0043] The cell engine performance was evaluated like Example 1 using the 0.03OLiNi_{0.75}Co_{0.22}Ti₂ above-mentioned powder. Consequently, the initial discharge capacity in 2.5-4.3V was 187 mAh/g, the initial discharge average electrical potential difference was 3.795V, and the capacity after a 20 times charge-and-discharge cycle was 187 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 195 degrees C. Moreover, the diffraction full width at half maximum with the same said of LiNi_{0.75}Co_{0.22}Mg_{0.03}O₂ which was with the magnesium nitrate or the chromium nitrate instead of nitric-acid titanium, and LiNi_{0.75}Co_{0.22}Cr_{0.03}O₂ was obtained, and the outstanding cell property was acquired.

[Example 5] As well as Example 1, each ammine complex of cobalt was mixed with nickel, the salt (a nickel:Co atomic ratio is 0.8:0.2) and lithium-hydroxide 1 hydrate powder which were obtained by making 100-150 degrees C heat this under the pressure of one to 5 atmospheric pressure were mixed, and the sheath which consists of mullite-cordierite system refractories was filled up. The above-mentioned sheath with which it filled up with raw material powder was continuously supplied to the same roller hearth kiln as Example 1, it held to it at 490 degrees C

for 1 hour, and preceding paragraph baking was performed to it. The programming rate to 490 degrees C was 400 degrees C/o'clock in temperature fall rate from 100 degrees C /and 490 degrees C to 200 degrees C o'clock from the room temperature.

[0044] Fine particles were taken out from the sheath after preceding paragraph baking, and the sheath was again filled up with the fine particles after preceding paragraph baking after re-mixing. Using the same roller hearth kiln as Example 1, a temperature-distribution setup from an inlet port to an outlet and the speed of supply of a sheath were changed, the sheath was supplied continuously, under the oxygen-nitrogen air current of oxygen 40 volume %, it held at 790 degrees C for 2 hours, and latter-part baking was performed. The programming rate from a room temperature to 790 degrees C was carried out in 200 degrees C/o'clock, and the temperature fall rate from 790 degrees C to 200 degrees C was carried out in 150 degrees C/o'clock. The X diffraction which used CuK alpha rays about 0.20OLiNi0.80Co2 powder was measured like Example 1. The diffraction full width at half maximum based on a field (110) in $2\theta=65^{\circ}$ degree of this X diffraction was 0.142 degrees.

[0045] As a result of evaluating the cell engine performance like Example 1 using the 0.20OLiNi0.80Co2 above-mentioned powder, the initial discharge capacity in 2.5-4.3V was 198 mAh/g, the initial discharge average electrical potential difference was 3.760V, and the capacity after a 20 times charge-and-discharge cycle was 197 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 183 degrees C.

[Example 6] As well as Example 1, each ammine complex of cobalt was mixed with nickel, the salt (the atomic ratio of nickel:Co is 0.8:0.2) and lithium-hydroxide 1 hydrate powder which were obtained by making 100-150 degrees C heat this under the pressure of one to 5 atmospheric pressure were mixed, and the sheath which consists of mullite-cordierite system refractories was filled up. The laminating of the above-mentioned sheath with which the quiescence furnace with height of 2.8m, a width of face [of 2.8m], and a depth of 2.8m was filled up with raw material powder was carried out, it held at 515 degrees C for 18 hours, and preceding paragraph baking was performed. The temperature fall time amount from 30 degrees C /and 515 degrees C to 200 degrees C of the programming rate to 515 degrees C was 5 hours (63 degrees C/o'clock in temperature fall rate) o'clock from the room temperature.

[0046] Fine particles were taken out from the sheath after preceding paragraph baking, and the sheath was again filled up with the fine particles after preceding paragraph baking after re-mixing. Using the same quiescence furnace as the above, the laminating of the sheath was carried out, under the oxygen-nitrogen air current containing oxygen 40 volume %, it held at 770 degrees C for 35 hours, and latter-part baking was performed. The programming rate from a room temperature to 770 degrees C was carried out in 70 degrees C/o'clock, and the temperature fall rate from 770 degrees C to 200 degrees C was carried out in 60 degrees C/o'clock.

[0047] The X diffraction which used CuK alpha rays as well as Example 1 about 0.20OLiNi0.80Co2 obtained powder was measured. The diffraction full width at half maximum based on a field (110) in $2\theta=65^{\circ}$ degree of this X diffraction was 0.125 degrees.

[0048] As a result of evaluating the cell engine performance like Example 1 using the 0.20OLiNi0.80Co2 above-mentioned powder, the initial discharge capacity in 2.5-4.3V was 187 mAh/g, the initial discharge average electrical potential difference was 3.730V, and the capacity after a 20 times charge-and-discharge cycle was 182 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 176 degrees C.

[Example 7] Each ammine complex of cobalt was mixed with nickel, the nickel-cobalt hydroxide

(the atomic ratio of nickel:Co is 0.8:0.2) and lithium-hydroxide 1 hydrate powder which heated and obtained the coprecipitate which carried out coprecipitation with carbon dioxide gas were mixed, and the sheath which consists of mullite-cordierite system refractories was filled up. The above-mentioned sheath with which it filled up with raw material powder was continuously supplied to the same roller hearth kiln as Example 1, it held to it at 515 degrees C for 5 hours, and preceding paragraph baking was performed to it. The temperature fall time amount from 50 degrees C /and 515 degrees C to 200 degrees C of the programming rate to 515 degrees C was 5 hours (63 degrees C/o'clock in temperature fall rate) o'clock from the room temperature.

[0049] Fine particles were taken out from the sheath after preceding paragraph baking, and the sheath was again filled up with the fine particles after preceding paragraph baking after re-mixing.

[0050] A temperature-distribution setup from an inlet port to an outlet and the speed of supply of a sheath were changed using the same roller hearth kiln as the above, the sheath filled up with the fine particles after preceding paragraph baking was supplied continuously, under the oxygen-nitrogen air current of oxygen 40 volume %, it held at 770 degrees C for 8 hours, and latter-part baking was performed. The temperature fall rate from 50 degrees C /and 770 degrees C to 200 degrees C of the programming rate from a room temperature to 770 degrees C was 63 degrees C/o'clock o'clock.

[0051] The X diffraction which used CuK alpha rays was measured about 0.20OLiNi0.80Co2 obtained powder like Example 1. The diffraction full width at half maximum based on a field (110) in 2theta=64**1 degree of this X diffraction was 0.118 degrees.

[0052] As a result of evaluating the cell engine performance using the 0.20OLiNi0.80Co2 above-mentioned powder, the initial discharge capacity in 2.5-4.3V was 182 mAh/g, the initial discharge average electrical potential difference was 3.715V, and the capacity after a 20 times charge-and-discharge cycle was 175 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 179 degrees C.

[Example 8] Each ammine complex of cobalt was mixed with nickel, the nickel-cobalt hydroxide (the atomic ratio of nickel:Co is 0.8:0.2) and lithium-hydroxide 1 hydrate powder which heated and obtained the coprecipitate which carried out coprecipitation with carbon dioxide gas were mixed, and the sheath which consists of mullite-cordierite system refractories was filled up. The above-mentioned sheath was continuously supplied to the same roller hearth kiln as Example 1, it held to it at 515 degrees C for 5 hours, and preceding paragraph baking was performed to it. The temperature fall time amount from 50 degrees C /and 515 degrees C to 200 degrees C of the programming rate to 515 degrees C was 5 hours (63 degrees C/o'clock in temperature fall rate) o'clock from the room temperature.

[0053] Fine particles were taken out from the sheath after preceding paragraph baking, and the sheath was again filled up with the fine particles after preceding paragraph baking after re-mixing. The sum total time amount of preceding paragraph baking was 20 hours. A temperature-distribution setup from an inlet port to an outlet and the speed of supply of a sheath were changed using the same roller hearth kiln as the above, the sheath filled up with the fine particles after preceding paragraph baking was supplied continuously, under the oxygen-nitrogen air current containing oxygen 40 volume %, it held at 750 degrees C for 1 hour, and latter-part baking was performed. The programming rate from a room temperature to 750 degrees C was carried out in 50 degrees C/o'clock, and the temperature fall rate from 750 degrees C to 200 degrees C was carried out in 63 degrees C/o'clock.

[0054] The X diffraction spectrum which used CuK alpha rays was measured about 0.20OLiNi0.80Co2 obtained powder like Example 1. The diffraction full width at half maximum

based on a field (110) in $2\theta = 65^\circ$ of this X diffraction was 0.215 degrees.

[0055] As a result of evaluating the cell engine performance using the $0.20\text{LiNi}_{0.80}\text{Co}_2$ above-mentioned powder, the initial discharge capacity in 2.5-4.3V was 178 mAh/g, the initial discharge average electrical potential difference was 3.765V, and the capacity after a 20 times charge-and-discharge cycle was 177 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 179 degrees C.

[0056]

[Effect of the Invention] According to this invention, the efficient manufacture approach is offered by the lithium content multiple oxide used as positive active material of the lithium secondary battery with which are satisfied of each of a high initial cell capacity, high discharge average electrical potential differences, outstanding charge-and-discharge cycle endurance, and high safeties, and low cost.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the new positive active material for lithium secondary batteries which consists of a lithium content multiple oxide, and its manufacture approach.

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PRIOR ART

[Description of the Prior Art] The expectation for small, the nonaqueous electrolyte rechargeable battery which is lightweight and has a high energy consistency, especially a lithium secondary battery is growing as portable-izing of a device and cordless-ization progress in recent years. The multiple oxide of lithiums, such as LiCoO_2 , LiNiO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, LiMn_2O_4 , and LiMnO_2 , and transition metals is known by the positive active material for lithium secondary batteries. The lithium secondary battery which used for positive active material the rock salt stratified multiple oxide which made cobalt and nickel dissolve like $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ shows good reversibility in high electrical-potential-difference regions, such as 2.7-4.3V, while being able to attain 180 - 190 mAh/g and a comparatively high capacity consistency.

[0003] Adoption of the lithium-nickel-cobalt multiple oxide represented by $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ has started as an ingredient which can especially discover high capacity recently. These are used for positive active material and commercialization of the lithium secondary battery of the high voltage by using occlusion, the carbon material which can be emitted as a negative-electrode active material, and a high energy consistency is advanced in the lithium.

[0004] Conventionally as the manufacture approach of a rock salt stratified multiple oxide of having made cobalt and nickel dissolving like $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ A nickel-cobalt coprecipitate is mixed with a lithium compound. At a standing furnace The inside of air, How to heat at 920 degrees C for 3 hours (JP,1-129364,A), Mix a nickel-cobalt coprecipitate with a lithium compound and a temperature up is carried out the rate for 330-degree-C/using rotary kiln. The approach lower the temperature and a standing furnace performs this baking at 750 degrees C under an oxygen ambient atmosphere further for 4 to 20 hours after performing preliminary baking (JP,11-111290,A), After it mixes a nickel-cobalt coprecipitate with a lithium compound and a standing furnace performs preliminary baking at 500 degrees C for 5 hours, the temperature is lowered and the approach (JP,10-214624,A) a standing furnace performs this baking at 720 degrees C under an oxygen ambient atmosphere further for 10 hours etc. is proposed.

[0005] However, by the approach of perform preliminary baking or this baking using rotary kiln, since mixing of impurities, such as an alumina which be a wall ingredient by wear of rotary kiln in order to make solid-state powder flow within rotary kiln, be avoid, there be problems, such as elevated temperature degradation of wall ingredients, such as a problem that the charge and discharge cycle endurance of the lithium secondary battery which used the baking object for the active material be scarce, and an alumina of rotary kiln.

[0006] Moreover, by the industrial scale production which requires calcinating so much at once for a productivity drive, when a standing furnace performs preliminary baking or this baking, in order to lessen the problem which a lithium content multiple oxide with a sufficient property cannot manufacture easily since the temperature variation in the temperature up of solid-state powder and the lot at the time of a temperature fall is not avoided, and temperature variation, it is

necessary to make small a temperature up or a temperature fall rate. Consequently, a temperature up and temperature fall time amount become long, and there is a problem to which productivity falls remarkably.

[0007] Moreover, a proposal that it excels in high capacity and thermal stability also has the lithium content multiple oxide whose diffraction full width at half maximum based on the field in the X diffraction (003) which mixes the alkali coprecipitation hydroxide and lithium hydroxide of nickel salt and cobalt salt, heat-treats, and is acquired is 0.01-0.1 degrees (JP,9-129231,A). However, even if it was the lithium content multiple oxide with which it is obtained by the manufacture approach given [this] in an official report, and (003) the diffraction full width at half maximum based on a field has the above-mentioned range, capacity, a discharge average electrical potential difference, charge-and-discharge cycle endurance, and safety were still dissatisfied.

[0008]

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, the efficient manufacture approach is offered by the lithium content multiple oxide used as positive active material of the lithium secondary battery with which are satisfied of each of a high initial cell capacity, high discharge average electrical potential differences, outstanding charge-and-discharge cycle endurance, and high safeties, and low cost.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] As mentioned above, the lithium content multiple oxide manufactured by the conventional approach needed the further amelioration as positive active material for lithium secondary batteries in the initial capacity, the initial discharge average electrical potential difference, the charge-and-discharge cycle endurance, the safety, and productivity of a cell.

[0009] This invention has a big cell capacity, its discharge average electrical potential difference is high, is excellent in charge-and-discharge cycle endurance, and aims at offering the new positive active material for lithium secondary batteries which consists of a high lithium content multiple oxide and its manufacture approach of safety.

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MEANS

[Means for Solving the Problem] this invention person found out that the lithium content multiple oxide with which the diffraction full width at half maximum based on a field (110) in $2\theta = 65^\circ$ of the powder X diffraction which was expressed with the specific general formula and used CuK alpha rays has a specific value satisfied both a high initial cell capacity a high discharge average electrical potential difference the outstanding charge-and-discharge cycle endurance and high safety as positive active material of a lithium secondary battery.

[0011] In this way, this invention is a general formula and $\text{LiNi}_x\text{Co}_y\text{M}_z\text{O}_2$ (however, M). At least one sort of elements chosen from aluminum, Mn, Ti, Mg, and Cr, It is expressed with $0.95 \leq x+y+z \leq 1.05$, $0.5 \leq x \leq 0.9$, $0.05 \leq y \leq 0.3$, and $0 \leq z \leq 0.2$. And the diffraction full width at half maximum based on the field in $2\theta = 65^\circ$ (110) of the powder X diffraction which used CuK alpha rays is in the positive active material for lithium secondary batteries characterized by consisting of a lithium content multiple oxide which is 0.13-0.20 degrees.

[0012] Below, this invention is explained further at a detail.

[0013]

[Embodiment of the Invention] In this invention, the lithium content multiple oxide which constitutes the positive active material of a lithium secondary battery is expressed with a general formula and $\text{LiNi}_x\text{Co}_y\text{M}_z\text{O}_2$. In here, M is a kind of element chosen from aluminum, Mn, Ti, Cr, and Mg at least. x, y and z are chosen, respectively so that $0.95 \leq x+y+z \leq 1.05$, $0.5 \leq x \leq 0.9$, $0.05 \leq y \leq 0.3$, and $0 \leq z \leq 0.2$ may be satisfied.

[0014] In the above, even when M is not contained by $z = 0$, the initial capacity of a cell is high and its charge-and-discharge cycle stability is high. z is not 0, when M is aluminum, compared with additive-free [of M] ($z = 0$), the charge-and-discharge cycle stability of a cell is still higher, there are few capacity falls in rapid charge and discharge, exoergic temperature is high, and safety is still higher. z is not 0, when M is Mn, compared with additive-free [of M], the exoergic temperature of a cell is high and safety is still higher. Furthermore, z is not 0, when M is Ti, Cr, or Mg, compared with additive-free [those], the charge-and-discharge cycle stability of a cell is high, and discharge voltage is also high. Especially, in this invention, a kind of element of aluminum and Mn of M is desirable at least.

[0015] In the above, the initial capacity of a cell falls that x is less than 0.5 about x, and y and z. If 0.9 is exceeded, the thermal stability of a cell will fall or charge-and-discharge cycle endurance will fall. Preferably, it is $0.60 \leq x \leq 0.85$. Since the thermal stability of a cell falls that y is less than 0.05 or charge-and-discharge cycle endurance falls, it is not desirable. If 0.3 is exceeded, the initial capacity of a cell will fall. Preferably, it is $0.10 \leq y \leq 0.20$. Moreover, although z is based also on an alloying element, it is $0.005 \leq z \leq 0.10$ preferably.

[0016] Moreover, in the powder X diffraction for which the lithium content multiple oxide which is the positive active material of this invention used CuK alpha rays, the diffraction full width at half maximum based on a field (110) in $2\theta = 65^\circ$ has 0.13-0.20 degrees. (110) It is

thought that the diameter of microcrystal has the relation it is small unrelated, so that the diffraction full width at half maximum based on a field has large half-value width reflecting the diameter of microcrystal of a lithium content multiple oxide. (110) The charge-and-discharge cycle endurance of the cell used as positive active material as the diffraction full width at half maximum based on a field is less than 0.13 degrees, initial capacity, average discharge voltage, or safety falls. Moreover, if the diffraction full width at half maximum based on a field (110) exceeds 0.20 degrees, the initial capacity of a cell and safety will fall. Desirable half-value width is 0.14-0.17 degrees.

[0017] The lithium content multiple oxide which has the general formula and the specific X diffraction full width at half maximum of the above-mentioned specification in this invention is the following, and making and manufacturing is desirable. That is, preceding paragraph baking of the mixture of the salt or coprecipitate containing the salt containing nickel and cobalt, a coprecipitate or nickel, cobalt, and Element M, and a mixture with a lithium compound or a lithium compound and the compound containing Element M is carried out at 430-530 degrees C, and, subsequently latter-part baking is carried out at 700-850 degrees C. In the above, when Element M is not contained in a lithium multiple oxide, the mixture of the salt or coprecipitate containing nickel and cobalt, and a lithium compound is calcinated (when it is $z=0$).

[0018] When nickel, cobalt, and Element M are contained in the salt or coprecipitate containing the salt containing the above-mentioned nickel and cobalt, a coprecipitate or nickel, cobalt, and Element M, it is desirable that nickel, cobalt, and Element M are distributed over homogeneity. Moreover, with the salt containing the salt and nickel containing nickel and cobalt, cobalt, and Element M, a carbonate, a sulfate, a nitrate, complex salt, etc. are used preferably.

[0019] The salt or coprecipitate containing the salt containing these nickel and cobalt, a coprecipitate or nickel, cobalt, and Element M is preferably manufactured by the following approaches. for example, when a nickel chloride, a cobalt chloride, and Element M are included Each chloride of Element M is made to dissolve in the water solution which saturated carbon dioxide gas. When the approach of adding and carrying out coprecipitation of the sodium-hydrogencarbonate solution, and drying it, the same nickel as the above, cobalt, and Element M are included 100-150 degrees C is made to heat the ammine complex mixed water solution containing Element M by the pressure of one to 5 atmospheric pressure the approach and nickel which are made to add and carry out coprecipitation of the alkali to the water solution containing each chloride of Element M, and are dried, cobalt, and if needed, and the approach of drying is adopted.

[0020] The approach of mixing the water solution which contains the salt or coprecipitate containing nickel and cobalt, and the compound of Element M when not using the salt or coprecipitate containing nickel, cobalt, and Element M, mixing a lithium compound further, and above, drying by the case where Element M is contained in a lithium content multiple oxide, is adopted preferably. Moreover, even when using the salt or coprecipitate containing nickel, cobalt, and Element M, it may mix with the water solution which contains the compound of Element M further, and Element M may be filled up. As a lithium compound mixed to the salt or coprecipitate containing the element M contained nickel, cobalt, and if needed, a lithium hydroxide, a lithium carbonate, lithium oxide, etc. are used preferably.

[0021] Subsequently the mixture of the salt or coprecipitate which contains Element M by this invention nickel, cobalt, and if needed, and a lithium compound is calcinated. It is required to perform baking by preceding paragraph baking in a specific temperature requirement and latter-part baking of each above. Baking of the preceding paragraph and the latter part may be plural [two or more steps of], respectively. If one of one-step baking is performed instead of two-step baking with the above-mentioned preceding paragraph and the latter part, the property used as the positive active material of the obtained lithium content multiple oxide, the initial capacity

which is specifically a cell, charge-and-discharge cycle endurance, safety, average discharge voltage, etc. will fall. Even if it is in two-step baking, when the temperature of preceding paragraph baking exceeds less than 430 degrees C or 530 degrees C or the temperature of latter-part baking exceeds less than 700 degrees C or 850 degrees C, the property as positive active material of the lithium content multiple oxide obtained like the above, i.e., initial capacity, charge-and-discharge cycle endurance, safety, average discharge voltage, a rapid charge-and-discharge property, etc. fall.

[0022] Moreover, it is desirable that the holding time [in / in preceding paragraph baking / the above-mentioned burning temperature] is 0.3 - 3 hours in this invention, and 0.5 - 2 hours is especially suitable. Moreover, the temperature fall rate (rate at which the temperature of a furnace descends from burning temperature to 200 degrees C) in preceding paragraph baking has desirable o'clock in 200-600 degrees C /, and o'clock is suitable for it in 300-500 degrees C /especially. The reaction of the powder and lithium compound which make nickel and cobalt a subject to preceding paragraph firing time being less than 0.3 hours is inadequate, and since the initial capacity of the lithium secondary battery using the obtained lithium content multiple oxide as positive active material falls, it is not desirable. On the other hand, if firing time exceeds 3 hours, since the productivity of a cell will fall, it is not desirable. It becomes [the diameter of a crystal of a lithium content multiple oxide] large that this temperature fall rate is less than 200 degrees C/o'clock to that programming rate hardly doing effect in preceding paragraph baking and is not desirable. Since a quick cooling facility is needed in large scale production when a temperature fall rate exceeds o'clock in 600 degrees C /and an installation cost and a running cost become high on the other hand, it is not desirable. Furthermore, as for latter-part baking, it is desirable that the holding time in the above-mentioned burning temperature is 1 - 4 hours in this invention, and 1 - 2.5 hours is suitable for it especially. Moreover, the temperature fall rate (rate at which the temperature of a furnace descends from burning temperature to 200 degrees C) in latter-part baking has desirable o'clock in 100-500 degrees C /, and o'clock is suitable for it in 200-400 degrees C /especially. Since the shift reaction to the layer structure containing the lithium of the powder and lithium compound which make nickel and cobalt a subject to the above-mentioned firing time being less than 1 hour is inadequate, it is not desirable. When the above-mentioned firing time exceeds 4 hours, as a result of a crystal's growing on the other hand, since the engine performance as positive active material of the obtained lithium content multiple oxide falls and the productivity of a lithium content multiple oxide falls, it is not desirable. To that programming rate hardly doing effect, the diameter of a crystal of a lithium content multiple oxide size-comes that this temperature fall rate is less than 100 degrees C/o'clock, and latter-part baking also comes. Since a quick cooling facility is needed in large scale production when a temperature fall rate exceeds o'clock in 300 degrees C /or more and an installation cost and a running cost become high on the other hand, it is not desirable.

[0023] It is desirable to perform above-mentioned preceding paragraph baking and above-mentioned latter-part baking in oxygen content gas, and although especially the oxygen density in preceding paragraph baking is not made an issue of, it is appropriate for it to carry out in atmospheric air. On the other hand, as for latter-part baking, it is desirable to carry out in the high oxygen content gas of an oxygen density. The oxygen density of latter-part baking has desirable 19 - 100 volume %, and 25 - 50 volume % is especially suitable for it. Since the engine performance as positive active material of the lithium content multiple oxide obtained when the oxygen density in this latter-part baking was low falls, it is not desirable.

[0024] As a means to carry out the above-mentioned preceding paragraph baking and latter-part baking of this invention on a scale of industry, although rotary kiln, a continuous furnace, a roller hearth kiln, etc. are mentioned, rotary kiln is deficient in the endurance of the mixing problem to the product of the component, or a kiln wall by wear of a kiln wall, and since there is a dust

processing problem in an outlet in being rapid baking, it is not desirable. In processing a lot of fine particles on a scale of industry, as a result of being hard to make temperature distribution into homogeneity, since the engine performance as positive active material of the obtained lithium content multiple oxide is inferior, a continuous furnace is not desirable.

[0025] On the other hand, a roller hearth kiln is equipment which is filled up with the powder which should be calcinated to the sheath which consists of refractories, throws a sheath into a tunnel-like furnace continuously, and carries out continuation baking of the rotation roller top when a sheath moves. Also in a rapid temperature up or a rapid temperature fall, a roller hearth kiln is excellent in especially the property as positive active material of the lithium content compound oxidation acquired since the temperature distribution in a sheath were made to homogeneity, and since productivity is high, it is desirable. Since this has uniform temperature distribution, it is because the diameter of average microcrystal is controllable. Although it is suitable for each of preceding paragraph baking and latter-part baking to carry out by the roller hearth kiln, it is appropriate preferably the either and to carry out latter-part baking by the roller hearth kiln.

[0026] In this invention, the positive electrode used as the positive active material of the above-mentioned lithium content multiple oxide is manufactured as follows preferably. namely, the thing for which carbon system electric conduction material and binding material, such as acetylene black, a graphite, and KETCHIEN black, are mixed to the powder of the above-mentioned lithium content multiple oxide -- a positive electrode -- a mixture is formed.

[0027] the above-mentioned positive electrode -- a mixture and this positive electrode -- a mixture -- the slurry or kneading object which consists of the inner solvent or inner dispersion medium of binding material -- positive-electrode charge collectors, such as aluminium foil and a stainless steel foil, -- spreading -- and/or, you make it support and it considers as a positive-electrode plate. Polyvinylidene fluoride, polytetrafluoroethylene, a polyamide, a carboxymethyl cellulose, acrylic resin, etc. are used for binding material. Porosity polyethylene, a porosity polypropylene film, etc. are used for a separator.

[0028] As a solvent of the electrolytic solution used for the lithium secondary battery which uses the lithium content multiple oxide of this invention as positive active material, a carbonate is desirable. a carbonate -- the shape of annular and a chain -- all can be used. As an annular carbonate, propylene carbonate, ethylene carbonate (henceforth EC), etc. are illustrated. As a chain-like carbonate, dimethyl carbonate, diethyl carbonate (henceforth DEC), ethyl methyl carbonate, methylpropyl carbonate, methyl isopropyl carbonate, etc. are illustrated.

[0029] In this invention, it is independent about the above-mentioned carbonate, or two or more sorts can be mixed and used. Moreover, you may use it, mixing with other solvents. Moreover, if a chain-like carbonate and an annular carbonate are used together depending on the ingredient of a negative-electrode active material, a discharge property, cycle endurance, and charge-and-discharge effectiveness may be improvable. Moreover, it is good also as a gel polymer electrolyte by adding the solute which adds a vinylidene fluoride-hexafluoropropylene copolymer (for example, "KAINA" Atochem trade name) and the vinylidene fluoride-perfluoro (propyl vinyl ether) copolymer indicated by JP,10-294131,A, and carries out a postscript to these organic solvents.

[0030] It is desirable to use any one or more sorts of the lithium salt which makes an anion ClO_4^- , CF_3SO_3^- , BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , CF_3CO_2^- , $2(\text{CF}_3\text{SO}_2)\text{N}^-$, etc. as a solute which constitutes the electrolytic solution used for this invention. As for an above-mentioned electrolytic solution or an above-mentioned polymer electrolyte, it is desirable to add the electrolyte which consists of lithium salt by the concentration of 0.2-2.0 mols/l. to said solvent or a solvent content polymer. If it deviates from this range, ionic conductivity will fall and the electrical conductivity of an electrolytic solution will fall. L. is especially selected in 0.5-1.5

mols /preferably.

[0031] The negative-electrode active material in the lithium secondary battery of this invention is the ingredient which emits [occlusion and] a lithium ion. Although especially the ingredient that forms these negative-electrode active materials is not limited, carbon compounds, such as an oxide which made the subject the metal of 14 or 15 groups of a lithium metal, a lithium alloy, a carbon material, and the periodic table, for example, a silicon carbide compound, and a boron carbide compound, a silicon oxide compound, a titanium sulfide, etc. are mentioned. As a carbon material, the pyrolysis object of the organic substance, an artificial graphite, a natural graphite, an earthy graphite, expanded graphite, a scale-like graphite, etc. can be used. Moreover, the compound which makes the tin oxide a subject can be used as an oxide. Copper foil, a nickel foil, etc. are used as a negative-electrode charge collector.

[0032] When an active material is a carbon material etc., as for the negative electrode used by this invention, it is desirable to knead with an organic solvent, to consider as a slurry, to apply, dry or press and to manufacture this slurry to a metallic foil charge collector. There is especially no constraint in the configuration of a lithium cell. The shape of a sheet (the shape of so-called film), the letter of folding, a winding mold closed-end cylindrical shape, a carbon button form, etc. are chosen according to an application.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Although an example explains this invention concretely below, this invention is not limited to these examples. In addition, Example 6 - Example 8 are examples of a comparison of this invention.

[Example 1] Each ammine complex of cobalt was mixed with nickel, the nickel which heated this at 100-150 degrees C under the pressure of one to 5 atmospheric pressure, and was obtained, the salt (atomic ratio 0.8:0.2 of nickel:Co) containing cobalt, and lithium-hydroxide 1 hydrate powder were mixed, and the sheath (at outside **, it is die-length [of 300mm] x width-of-face [of 300mm] x height of 80mm) which consists of mullite-cordierite system refractories was filled up. The above-mentioned sheath with which it filled up with raw material powder was continuously supplied to the roller hearth kiln (the overall length of 15m, height of 1.8m, width of face of 1.8m), was held at 515 degrees C for 30 minutes, and preceding paragraph baking was performed. The temperature fall time amount from 100 degrees C /and 515 degrees C to 200 degrees C of the programming rate from a room temperature to 515 degrees C was 40 minutes (470 degrees C/o'clock in temperature fall rate) o'clock.

[0034] After preceding paragraph baking, fine particles were taken out from the sheath and the sheath was again filled up with the fine particles after preceding paragraph baking after re-mixing. Using the same roller hearth kiln as the above, a temperature-distribution setup from an inlet port to an outlet and the speed of supply of a sheath were changed, the sheath was supplied continuously, under the oxygen-nitrogen air current containing oxygen 40 volume %, it held at 770 degrees C for 1.5 hours, and latter-part baking was performed. The temperature fall rate from 400 degrees C /and 770 degrees C to 200 degrees C of the programming rate from a room temperature to 770 degrees C was 350 degrees C/o'clock o'clock.

[0035] Thus, about 0.20OLiNi0.80Co2 obtained powder, the X diffraction was measured by CuKalpha using Rigaku RINT2100 mold X-ray diffractometer. The diffraction full width at half maximum based on a field (110) in 2theta=65**1 degree of this X diffraction was 0.148 degrees.

[0036] The 0.20OLiNi0.80Co2 above-mentioned powder, acetylene black, and polytetrafluoroethylene powder were mixed by the weight ratio of 80/16/4, and it kneaded, fabricated and dried, adding toluene, and the positive-electrode plate with a thickness of 150 micrometers was manufactured. Aluminium foil with a thickness of 20 micrometers is used as a positive-electrode charge collector, a metal lithium foil with a thickness of 500 micrometers is used for a separator at a negative electrode using porosity polypropylene with a thickness of 25 micrometers, a nickel foil with a thickness of 20 micrometers is used for a negative-electrode charge collector, the solution which contains LiPF6 in the mixed solvent of EC and DEC1:1 by the concentration of one mol is used for the electrolytic solution, and it is ***** in an argon glove compartment about the simple sealing cel (cell) made from stainless steel.

[0037] The above-mentioned cel was charged to 4.3V by the positive-electrode area per two and

0.2mA of constant current of 1cm, and while discharging to 2.5V in 0.2mA of constant current and calculating initial discharge capacity subsequently, the charge-and-discharge cycle trial was performed 20 times. The initial discharge capacity in 2.5-4.3V was 198 mAh/g, the initial discharge average electrical potential difference was 3.777V, and the capacity after a 20 times charge-and-discharge cycle was 198 mAh/g. Moreover, similarly, it charged to 4.3V by the positive-electrode area per two and 0.2mA of constant current of 1cm, the simple sealing cell made from stainless steel was disassembled in the argon glove compartment, the positive-electrode object sheet after charge was taken out, and it pierced in 3mm of diameters after washing the positive-electrode plate, and sealed to the aluminum capsule with EC, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 186 degrees C.

[Example 2] It dried, after mixing each ammine complex of cobalt with nickel and mixing the nickel obtained by making 100-150 degrees C heat this under the pressure of one to 5 atmospheric pressure, the salt containing cobalt, and an aluminium nitrate water solution, and fine particles were obtained by calcinating at 300 degrees C for 5 hours. Lithium-hydroxide 1 hydrate powder was mixed with these fine particles, the sheath with which the same roller hearth kiln as Example 1 was filled up with raw material powder was supplied continuously, and preceding paragraph baking and latter-part baking were performed on the same conditions as Example 1.

[0038] The X diffraction chart was measured about 0.03OLiNi0.8Co0.17aluminum2 obtained powder like Example 1. In this X diffraction, the diffraction full width at half maximum based on the field (110) near $2\theta=65^\circ$ was 0.168 degrees.

[0039] The cell engine performance was evaluated like Example 1 using the 0.03OLiNi0.8Co0.17aluminum2 above-mentioned powder. Consequently, the initial discharge capacity in 2.5-4.3V was 188 mAh/g, the initial discharge average electrical potential difference was 3.770V, and the capacity after a 20 times charge-and-discharge cycle was 185 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 192 degrees C.

[Example 3] It dried, after mixing the nickel-cobalt coprecipitation hydroxide and manganese nitrate water solution which heated and obtained the coprecipitate to which coprecipitation of the water solution containing each chloride of nickel and cobalt was carried out with alkali, and fine particles were obtained by calcinating at 300 degrees C for 5 hours.

[0040] Lithium-hydroxide 1 hydrate powder was mixed with these fine particles, the sheath with which the same roller hearth kiln as Example 1 was filled up with raw material powder was supplied continuously, and preceding paragraph baking and latter-part baking were performed on the same conditions as Example 1. About 0.06OLiNi0.76Co0.18Mn2 obtained powder, like Example 1, CuK alpha rays were used and the X diffraction was measured. The diffraction full width at half maximum based on a field (110) in $2\theta=65^\circ$ of this X diffraction was 0.161 degrees.

[0041] The cell engine performance was evaluated like Example 1 using the 0.06OLiNi0.76Co0.18Mn2 above-mentioned powder. Consequently, the initial discharge capacity in 2.5-4.3V was 183 mAh/g, the initial discharge average electrical potential difference was 3.767V, and the capacity after a 20 times charge-and-discharge cycle was 183 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 188 degrees C.

[Example 4] It dried, after mixing the nickel-cobalt coprecipitation hydroxide and nitric-acid

titanium water solution which heated and obtained the coprecipitate to which coprecipitation of the water solution containing each chloride of nickel and cobalt was carried out with alkali, and fine particles were obtained by calcinating at 300 degrees C for 5 hours.

[0042] Lithium-hydroxide 1 hydrate powder was mixed with these fine particles, the sheath with which the same roller hearth kiln as Example 1 was filled up with raw material powder was supplied continuously, and preceding paragraph baking and latter-part baking were performed on the same conditions as Example 1. Make it be the same as that of Example 1 about 0.03OLiNi0.75Co0.22Ti2 obtained powder. CuK alpha rays were used and the X diffraction was measured. The diffraction full width at half maximum based on a field (110) in $2\theta=65^\circ$ degree of this X diffraction was 0.162 degrees.

[0043] The cell engine performance was evaluated like Example 1 using the 0.03OLiNi0.75Co0.22Ti2 above-mentioned powder. Consequently, the initial discharge capacity in 2.5-4.3V was 187 mAh/g, the initial discharge average electrical potential difference was 3.795V, and the capacity after a 20 times charge-and-discharge cycle was 187 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 195 degrees C. Moreover, the diffraction full width at half maximum with the same said of LiNi0.75Co0.22Mg 0.03O2 which was with the magnesium nitrate or the chromium nitrate instead of nitric-acid titanium, and LiNi0.75Co0.22Cr 0.03O2 was obtained, and the outstanding cell property was acquired.

[Example 5] As well as Example 1, each ammine complex of cobalt was mixed with nickel, the salt (a nickel:Co atomic ratio is 0.8:0.2) and lithium-hydroxide 1 hydrate powder which were obtained by making 100-150 degrees C heat this under the pressure of one to 5 atmospheric pressure were mixed, and the sheath which consists of mullite-cordierite system refractories was filled up. The above-mentioned sheath with which it filled up with raw material powder was continuously supplied to the same roller hearth kiln as Example 1, it held to it at 490 degrees C for 1 hour, and preceding paragraph baking was performed to it. The programming rate to 490 degrees C was 400 degrees C/o'clock in temperature fall rate from 100 degrees C /and 490 degrees C to 200 degrees C o'clock from the room temperature.

[0044] Fine particles were taken out from the sheath after preceding paragraph baking, and the sheath was again filled up with the fine particles after preceding paragraph baking after re-mixing. Using the same roller hearth kiln as Example 1, a temperature-distribution setup from an inlet port to an outlet and the speed of supply of a sheath were changed, the sheath was supplied continuously, under the oxygen-nitrogen air current of oxygen 40 volume %, it held at 790 degrees C for 2 hours, and latter-part baking was performed. The programming rate from a room temperature to 790 degrees C was carried out in 200 degrees C/o'clock, and the temperature fall rate from 790 degrees C to 200 degrees C was carried out in 150 degrees C/o'clock. The X diffraction which used CuK alpha rays about 0.20OLiNi0.80Co2 powder was measured like Example 1. The diffraction full width at half maximum based on a field (110) in $2\theta=65^\circ$ degree of this X diffraction was 0.142 degrees.

[0045] As a result of evaluating the cell engine performance like Example 1 using the 0.20OLiNi0.80Co2 above-mentioned powder, the initial discharge capacity in 2.5-4.3V was 198 mAh/g, the initial discharge average electrical potential difference was 3.760V, and the capacity after a 20 times charge-and-discharge cycle was 197 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 183 degrees C.

[Example 6] As well as Example 1, each ammine complex of cobalt was mixed with nickel, the salt (the atomic ratio of nickel:Co is 0.8:0.2) and lithium-hydroxide 1 hydrate powder which

were obtained by making 100-150 degrees C heat this under the pressure of one to 5 atmospheric pressure were mixed, and the sheath which consists of mullite-cordierite system refractories was filled up. The laminating of the above-mentioned sheath with which the quiescence furnace with height of 2.8m, a width of face [of 2.8m], and a depth of 2.8m was filled up with raw material powder was carried out, it held at 515 degrees C for 18 hours, and preceding paragraph baking was performed. The temperature fall time amount from 30 degrees C /and 515 degrees C to 200 degrees C of the programming rate to 515 degrees C was 5 hours (63 degrees C/o'clock in temperature fall rate) o'clock from the room temperature.

[0046] Fine particles were taken out from the sheath after preceding paragraph baking, and the sheath was again filled up with the fine particles after preceding paragraph baking after re-mixing. Using the same quiescence furnace as the above, the laminating of the sheath was carried out, under the oxygen-nitrogen air current containing oxygen 40 volume %, it held at 770 degrees C for 35 hours, and latter-part baking was performed. The programming rate from a room temperature to 770 degrees C was carried out in 70 degrees C/o'clock, and the temperature fall rate from 770 degrees C to 200 degrees C was carried out in 60 degrees C/o'clock.

[0047] The X diffraction which used CuK alpha rays as well as Example 1 about 0.20OLiNi0.80Co2 obtained powder was measured. The diffraction full width at half maximum based on a field (110) in $2\theta = 65^{\circ} \pm 1$ degree of this X diffraction was 0.125 degrees.

[0048] As a result of evaluating the cell engine performance like Example 1 using the 0.20OLiNi0.80Co2 above-mentioned powder, the initial discharge capacity in 2.5-4.3V was 187 mAh/g, the initial discharge average electrical potential difference was 3.730V, and the capacity after a 20 times charge-and-discharge cycle was 182 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 176 degrees C.

[Example 7] Each ammine complex of cobalt was mixed with nickel, the nickel-cobalt hydroxide (the atomic ratio of nickel:Co is 0.8:0.2) and lithium-hydroxide 1 hydrate powder which heated and obtained the coprecipitate which carried out coprecipitation with carbon dioxide gas were mixed, and the sheath which consists of mullite-cordierite system refractories was filled up. The above-mentioned sheath with which it filled up with raw material powder was continuously supplied to the same roller hearth kiln as Example 1, it held to it at 515 degrees C for 5 hours, and preceding paragraph baking was performed to it. The temperature fall time amount from 50 degrees C /and 515 degrees C to 200 degrees C of the programming rate to 515 degrees C was 5 hours (63 degrees C/o'clock in temperature fall rate) o'clock from the room temperature.

[0049] Fine particles were taken out from the sheath after preceding paragraph baking, and the sheath was again filled up with the fine particles after preceding paragraph baking after re-mixing.

[0050] A temperature-distribution setup from an inlet port to an outlet and the speed of supply of a sheath were changed using the same roller hearth kiln as the above, the sheath filled up with the fine particles after preceding paragraph baking was supplied continuously, under the oxygen-nitrogen air current of oxygen 40 volume %, it held at 770 degrees C for 8 hours, and latter-part baking was performed. The temperature fall rate from 50 degrees C /and 770 degrees C to 200 degrees C of the programming rate from a room temperature to 770 degrees C was 63 degrees C/o'clock o'clock.

[0051] The X diffraction which used CuK alpha rays was measured about 0.20OLiNi0.80Co2 obtained powder like Example 1. The diffraction full width at half maximum based on a field (110) in $2\theta = 64^{\circ} \pm 1$ degree of this X diffraction was 0.118 degrees.

[0052] As a result of evaluating the cell engine performance using the 0.20OLiNi0.80Co2 above-mentioned powder, the initial discharge capacity in 2.5-4.3V was 182 mAh/g, the initial

discharge average electrical potential difference was 3.715V, and the capacity after a 20 times charge-and-discharge cycle was 175 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 179 degrees C.

[Example 8] Each ammine complex of cobalt was mixed with nickel, the nickel-cobalt hydroxide (the atomic ratio of nickel:Co is 0.8:0.2) and lithium-hydroxide 1 hydrate powder which heated and obtained the coprecipitate which carried out coprecipitation with carbon dioxide gas were mixed, and the sheath which consists of mullite-cordierite system refractories was filled up. The above-mentioned sheath was continuously supplied to the same roller hearth kiln as Example 1, it held to it at 515 degrees C for 5 hours, and preceding paragraph baking was performed to it. The temperature fall time amount from 50 degrees C /and 515 degrees C to 200 degrees C of the programming rate to 515 degrees C was 5 hours (63 degrees C/o'clock in temperature fall rate) o'clock from the room temperature.

[0053] Fine particles were taken out from the sheath after preceding paragraph baking, and the sheath was again filled up with the fine particles after preceding paragraph baking after re-mixing. The sum total time amount of preceding paragraph baking was 20 hours. A temperature-distribution setup from an inlet port to an outlet and the speed of supply of a sheath were changed using the same roller hearth kiln as the above, the sheath filled up with the fine particles after preceding paragraph baking was supplied continuously, under the oxygen-nitrogen air current containing oxygen 40 volume %, it held at 750 degrees C for 1 hour, and latter-part baking was performed. The programming rate from a room temperature to 750 degrees C was carried out in 50 degrees C/o'clock, and the temperature fall rate from 750 degrees C to 200 degrees C was carried out in 63 degrees C/o'clock.

[0054] The X diffraction spectrum which used CuK alpha rays was measured about 0.20OLiNi0.80Co2 obtained powder like Example 1. The diffraction full width at half maximum based on a field (110) in $2\theta = 65^{\circ} \pm 1$ degree of this X diffraction was 0.215 degrees.

[0055] As a result of evaluating the cell engine performance using the 0.20OLiNi0.80Co2 above-mentioned powder, the initial discharge capacity in 2.5-4.3V was 178 mAh/g, the initial discharge average electrical potential difference was 3.765V, and the capacity after a 20 times charge-and-discharge cycle was 177 mAh/g. Moreover, like Example 1, the temperature up was carried out the rate for 5-degree-C/with the scanning differential calorimeter, and exoergic initiation temperature was measured. Consequently, exoergic initiation temperature was 179 degrees C.

[Translation done.]